

The University of Chicago

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CYCLOPROPANE WITH BROMINE AND WITH
HYDROGEN BROMIDE
- II. THE OXYGEN EFFECT IN THE REACTION OF
BROMINE WITH NEOPENTANE, *TERT*-BUTYL-
BENZENE AND TRIMETHYLACETIC ACID

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
JUNE, 1941

By
MORTON Z. FINEMAN

CHICAGO, ILLINOIS

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THE OXYGEN EFFECT IN THE REACTION OF CYCLOPROPANE
WITH BROMINE AND WITH HYDROGEN BROMIDE

Previous papers from this laboratory^{1,2,3} have shown that the bromination of toluene and phenanthrene are markedly accelerated by traces of oxygen and peroxides. These and similar observations with other hydrocarbons⁴ have led to a re-examination of the reactions of cyclopropane with bromine and with hydrogen bromide.

PREVIOUS WORK

The literature on the reaction of cyclopropane with bromine and with hydrogen bromide is meager, although a great deal of work has been done on the cleavage of the carbon ring in substituted cyclopropanes.⁵ Gustavson⁶ states that, at ordinary temperatures, cyclopropane reacts with bromine quite slowly in the dark, but rapidly in the sunlight. He noted that, besides trimethylene bromide, propyl bromide, more highly brominated products and large amounts of hydrogen bromide were formed. Ogg and Priest⁷ have investigated several vapor phase reactions of cyclopropane. At 250° iodine yielded 1,3-diiodopropane; light had no

¹Kharasch, Margolis, White, and Mayo, J. Am. Chem. Soc., 59, 1405 (1937).

²Kharasch, White, and Mayo, J. Org. Chem., 2, 574 (1938).

³Kharasch, White, and Mayo, ibid., 3, 33 (1938).

⁴Hered, Ph.D. dissertation, University of Chicago.

⁵(a) Farmer, J. Chem. Soc., 123, 3341 (1923); (b) Demjanow and Dojarenko, Ber., 56B, 2200 (1923); (c) Nicolet and Sattler, J. Am. Chem. Soc., 49, 2066 (1927); (d) Bone and Perkin, J. Chem. Soc., 67, 118 (1895); (e) Gustavson, J. prakt. Chem. (2), 62, 270 (1900).

⁶Gustavson, ibid. (2), 62, 273 (1900).

⁷Ogg and Priest, J. Am. Chem. Soc., 60, 217 (1938).

effect on the reaction. At room temperature under intense illumination, bromine added to cyclopropane to give mainly 1,3-dibromopropane and a little hydrogen bromide. At 220° in the dark, large amounts of hydrogen bromide were formed. Hydrogen bromide and cyclopropane gave little indication of reaction at 300° .

EXPERIMENTAL PART

The cyclopropane used in this work was obtained from the Ohio Chemical Company. It boiled at -33.5° to -33° and was completely absorbed by concentrated sulfuric acid. The method of preparation excluded the possibility of the presence of propylene or similar impurities.⁸ Analytical reagent grade bromine was used. It was dried with anhydrous calcium bromide and distilled in an all glass apparatus. Only the middle fraction (boiling point 58.7° at 751 mm.) was used.

In the study of the addition of bromine and hydrogen bromide to cyclopropane, difficulty was experienced in obtaining consistent results until an apparatus was devised for eliminating dust and water from the reaction. The tube A (see Fig. 1) was

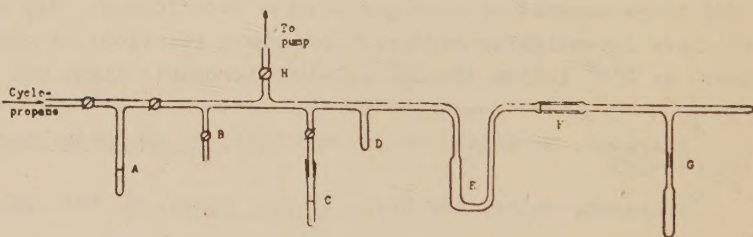


Fig. 1.

calibrated to contain 1.56 gram of liquid cyclopropane at the temperature of a carbon dioxide - acetone bath. The tube C, calibrated (by titration) to contain 0.288 or 2.62 grams of liquid hydrogen bromide at the bath temperature, was attached to the system by a ground glass connection. To avoid contact with stop-

⁸Haas, McBee, Hinds, and Gluesenkamp, Ind. Eng. Chem., 28, 1178 (1936).

cock and joint lubricant, bromine was weighed out in a tube which was then sealed to the line at D. The tube containing hydrogen bromide or bromine, after being thus attached to the system, was cooled in liquid nitrogen. The whole system then evacuated to about 10^{-5} mm. of mercury through the line H. By suitable manipulation of the stopcocks, cyclopropane was introduced into A, any excess hydrogen bromide or cyclopropane was removed from the calibrated tubes by cautious evacuation, and the reactants were degassed.³ They were then distilled through phosphorus pentoxide, a glass wool plug in tube E, and a glass filter cloth in tube F, into the reaction tube G. Any added substances were placed in G before it was sealed onto the system; they were kept cold during the above procedures. For experiments in the absence of oxygen (indicated by - in the oxygen columns of the tables), the system was then evacuated once more to remove traces of uncondensed gases, and tube G was sealed off at the constriction. For experiments in the presence of oxygen, the degassing operation was omitted and oxygen was admitted through stopcock B until its pressure in the line was 22 cm. before tube G was sealed off. Since this tube was at the temperature of liquid nitrogen, the pressure was estimated to increase to about one atmosphere at room temperature.

For the dark reaction, the bomb tubes were allowed to stand in an iron pipe at room temperature. In the photochemical studies (indicated by + in the light column in the tables) the reaction tubes were immersed in water kept at $20^{\circ} \pm 5^{\circ}$. Only the liquid phase was exposed to light from a 300-watt incandescent lamp placed at a distance of approximately ten centimeters.

After reaction, the bomb tube was immersed in liquid nitrogen and opened. A tube was then sealed on to the bomb so that at room temperature the low-boiling contents would distill into water or aqueous potassium iodide solution. The substance remaining in the bomb was washed into the same solution. Unreacted bromine or hydrogen bromide was then determined by titration.

Reaction of cyclopropane with bromine.--In Table 1 are summarized the experiments which demonstrate the effect of various substances on the interaction of bromine and cyclopropane. The first two show that the reaction of cyclopropane and bromine in the dark is very slow, and that oxygen has a slight accelerating effect. It is remarkable, however, that, in the absence of

TABLE 1
THE ADDITION OF BROMINE TO CYCLOPROPANE^a

Added Substances ^b	Conditions		Reaction Time	% Reaction ^c	Remarks
	Oxygen	Light			
None	-	-	52 days	13	2% HBr found
None	-	-	53 days	20	2% HBr found
None	-	+	200 hours	47	Checked. 8.3% HBr
None	+	+	1.9 hours	100	Checked
None*	+	+	2.0 hours	100	...
Ascaridole, 0.03	-	+	3.2 hours	100	...
Bz ₂ O ₂ , 0.03	-	+	3.5 hours	100	...
Bz ₂ O ₂ , 0.03	+	+	2.1 hours	100	...
i-AmONO, 0.1	+	+	204 hours	37	2% HBr found
Ethanol, 0.05	+	+	64 hours	100	...
Water, 0.1	+	+	1.7 hours	100	...
Water, 0.1	-	+	77 hours	100	...
Hydrogen bromide	+	+	2.1 hours	100	Checked. Two phases

^aIn every experiment save the one marked with an asterisk the mol ratio of bromine to cyclopropane was 1:10; in this one instance the mol ratio was 1:2. Experiments in concentrated solution were not carried out because under such conditions bromine seems to act as an inhibitor for chain reactions.

^bQuantities expressed in moles per mol of bromine used.

^cComplete reaction was assumed when the color faded to a faint yellow.

oxygen, the photochemical reaction is also extremely slow (47% reaction in 200 hours), whereas, in the presence of oxygen, the reaction is complete in two hours. Peroxides exert an effect similar to that of oxygen. Another important observation is the inhibition of the photochemical oxygen-catalyzed reaction by ethanol and isoamyl nitrite.

Reaction of cyclopropane with hydrogen bromide.--Two distinct types of reaction mixtures were used in the study of the reaction of cyclopropane and hydrogen bromide. In the first group of experiments, equimolecular quantities of the reactants were

TABLE 2

THE ADDITION OF HYDROGEN BROMIDE TO CYCLOPROPANE

Added Substances ^a	Conditions		% Reaction	Remarks
	Oxygen	Light		
None ^b	-	-	8	...
None ^b	-	+	11, 12	...
None ^b	+	-	81	...
None ^b	+	+	99, 99	...
Bz ₂ O ₂ , 0.03 ^b	-	+	74	...
Diphenylamine, 0.03 ^b	+	+	91	...
Catechol, 0.03 ^b	+	+	28, 41, 43 ^c	Catechol not completely dissolved
Catechol, 0.03 ^b	+	-	41, 50 ^c	
Catechol, 0.03 ^b	-	+	41, 43 ^c	
Water, 0.1 ^b	-	-	87	...
None ^d	-	-	55, 66 ^e	...
None ^d	-	+	70 ^c	...
None ^d	+	-	67, 73 ^e	...
None ^d	+	+	74, 76 ^e	...
Thiocresol, 0.03 ^d	-	+	90	Mixture became warm in a few minutes
Catechol, 0.03 ^d	-	-	97 ^c	
Water, 0.03 ^d	-	-	94	
Acetic acid, 0.03 ^d	-	-	87	

^aQuantities expressed in moles per mole of hydrogen bromide used.

^bMole ratio of hydrogen bromide to cyclopropane 1:10; reaction time, 2 hours.

^cOdor of product indicated formation of propyl ether of catechol.

^dMole ratio of hydrogen bromide to cyclopropane 1:1; reaction time, 4 hours.

^eAddition products combined and found to be normal propyl bromide.

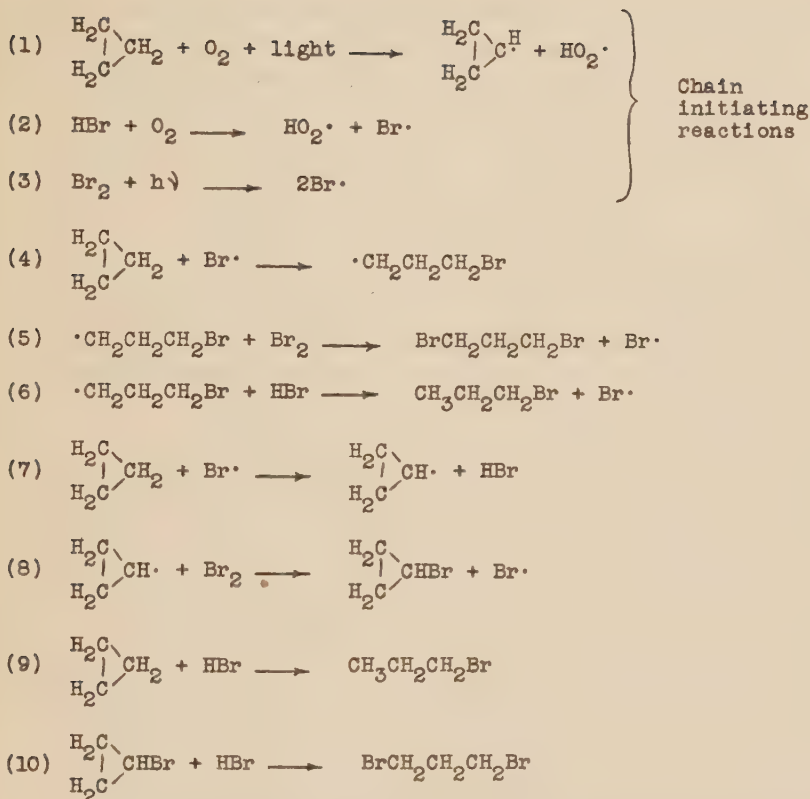
used, in the second a tenfold excess of cyclopropane. These two procedures gave strikingly different results (Table 2). Thus, when excess cyclopropane was used, and oxygen was removed from the system, a slow reaction took place in the dark (8% in two hours); only a slight increase was observed upon illumination (11% in two hours). However, in the presence of oxygen there was a tremendous increase in the reaction velocity. Thus, in two hours, 81% of normal propyl bromide was obtained in the dark and nearly 100% in the light. The effect of benzoyl peroxide on the rate of reaction was similar to that of oxygen. Antioxidants appear partially to overcome the accelerating effect of oxygen, but duplicate experiments show that, in illuminated reactions without oxygen, catechol is an accelerator. Since water has the same accelerating effect (in the dark), it seems probable that catechol accelerates the reaction by one mechanism while inhibiting it by a second.

On the other hand, when equimolar quantities of cyclopropane and hydrogen bromide are used, oxygen and illumination have no significant effect on the rate of reaction. Water, acetic acid, thiophenol and catechol accelerate the addition reaction in the absence of oxygen.

DISCUSSION

From the experiments cited, it is evident that pure cyclopropane and pure bromine do not react appreciably in the dark, and only very slowly in the light. The observations recorded in the literature regarding the ring cleavage by bromine must therefore apply to an oxygen-catalyzed photochemical reaction. A careful study of the data here given indicates that the reaction is a chain reaction similar to the oxygen-catalyzed photochemical brominations of phenanthrene² and toluene^{1,3}. In support of this conclusion the following facts may be cited: (1) minute amounts of oxygen or peroxides are effective in bringing about a rapid reaction; (2) traces of inhibitors markedly retard the reaction.

The following schematic representation is suggested for the bromination of cyclopropane; a dot is used to represent an unpaired electron.



The low-boiling products found could have been formed in reactions 6, 8, and 9; reaction 7 readily explains the formation of hydrogen bromide. The relatively small effect of light in the absence of oxygen is surprising, for, from equations 3, a fairly large concentration of bromine atoms might be expected. This small effect suggests that the active entity responsible for the chain reaction may be not the bromine atom but a free radical of the type $\cdot\text{BrO}_2$.

From the standpoint of the considerations just given, there is at once available an attractive explanation to account for the fact that cyclopropylamine does not react with bromine, although the carbon ring is easily cleaved by nitrous acid.⁹ The

⁹Kishner, *Chem. Zentr.*, 72, II, 579 (1901); 76, I, 1703 (1905).

amino group is an inhibitor in reactions involving bromine atoms. The stability of the ring, therefore, is to be ascribed to the chain-breaking mechanism of the amino group, rather than to the inherently greater stability of the ring in cyclopropylamine. The same explanation applies to the resistance toward cleavage of cyclopropyl cyanide.^{5c} The effect of side groups on the stability of the cyclopropane ring is, therefore, not necessarily related to ease of cleavage of the ring with bromine.

The oxygen effect in the reaction of hydrogen bromide and cyclopropane, when the latter is used in large excess, is readily explained by the bromine atom chain mechanism. The free bromine atoms are formed by equations 1 or 2. The formation of normal propyl bromide by the chain mechanism is indicated by equations 4 and 6; equation 9 shows a different mechanism.

The small effect of light and oxygen on the rate of reaction of equimolecular quantities of hydrogen bromide and cyclopropane suggests an ionic mechanism for this reaction. Furthermore, the fact that thiocresol, catechol, acetic acid, and water here have an accelerating effect lends support to the idea that the mechanism is ionic. These substances can all cause the hydrogen bromide molecule to dissociate into a bromide ion and a positively charged fragment. The cleavage of the cyclopropane ring by ions would not be expected to be photochemical. The accelerating effect of hydroxylic compounds indicates that, in concentrated hydrogen bromide solutions, the contribution of an atom mechanism to the rate of reaction is insignificant.

SUMMARY

1. The reaction of bromine with a tenfold excess of cyclopropane is greatly accelerated by the combined effect of oxygen and light.
2. The reaction of hydrogen bromide with a tenfold excess of cyclopropane is greatly accelerated by oxygen, but only slightly accelerated by light.
3. Organic peroxides have an effect similar to that of oxygen.
4. A chain mechanism involving bromine atoms is suggested for each addition reaction.
5. The addition of hydrogen bromide to an equivalent

quantity of cyclopropane is not significantly affected by oxygen or light, but is accelerated by hydroxylic compounds. For this effect a competing non-atomic mechanism is suggested.

THE OXYGEN EFFECT IN THE REACTION OF BROMINE
WITH NEOPENTANE, tert-BUTYLBENZENE
AND TRIMETHYLACETIC ACID

Preliminary work in this laboratory has shown that tertiary hydrogen atoms are more readily replaced by bromine atoms than are secondary hydrogen atoms.¹ Because of these observations, it was decided to investigate the bromination of compounds containing primary hydrogen atoms.

A search of the literature revealed that aliphatic compounds containing only primary hydrogen atoms have hitherto been brominated only at elevated temperatures. Most of the reactions were carried out in the gas phase.² The only reported low temperature liquid phase bromination of a compound containing primary hydrogen atoms is that of Colibasi petroleum boiling at 0-10°; this material contained neopentane, but the range of its boiling point indicates that it was a mixture of hydrocarbons.³ Moreover, although the refractive index of the reaction product agrees with that of neopentyl bromide (prepared by Whitmore, Whittle, and Harriman⁴), the large discrepancies in boiling point and in density suggest a mixture of brominated hydrocarbons.⁵ Because of these discrepancies, it was decided to reinvestigate the liquid phase bromination of neopentane, tert-butylbenzene and trimethylacetic acid.

¹Hered, Ph.D. dissertation, University of Chicago.

²(a) Egloff, Schaad and Lowry, Jr., Chem. Rev., 8, 58 (1931); (b) Perelis, Ind. Eng. Chem., 25, 1160 (1933).

³Poni, Chem. Zentr., 1906, I, 442.

⁴Whitmore, Whittle, and Harriman, J. Am. Chem. Soc., 61, 1585 (1939).

⁵Cf. the physical constants obtained by the two investigators:

Boiling Point	Density	n_D^{20}
89-91/749 mm.	1.260 ^{20.4} / ₀	1.4369 ³
105/732 mm.	1.199 ²⁰ / ₄	1.4370 ⁴

EXPERIMENTAL RESULTS

The results indicate that pure neopentane does not react with dilute solutions of bromine at room temperature even under optimum conditions, that is, in the presence of oxygen or peroxides and under illumination. At higher temperatures, the bromination, though still very slow, is accelerated by light, oxygen and peroxides. Reaction does not take place in the dark under any conditions here investigated. At 50°, ascaridol and lauroyl peroxide accelerate the reaction in the light either in the presence or in the absence of oxygen; these reagents have no effect.

TABLE 3

THE ADDITION OF BROMINE TO NEOPENTANE^{a, b, c}

Added Substances	Oxygen Pressure Cm. Hg	Light	Reaction Time Hours	Per Cent Reaction
None	vacuo	+	30	0
None	0.5	+	63	100
None	5	+	13	10
None	10	+	43	100
None	15	+	18	100
None	15	-	20	0
Ascaridole 0.01 ^d	vacuo	+	32	100
Ascaridole 0.01 ^d	5	+	12	100
Lauroyl peroxide 0.01 ^d	5	-	50	0
Lauroyl peroxide 0.01 ^d	5	+	21	100

^aThe mol ratio of bromine to neopentane was 1:44.

^bOther experiments where direct sunlight was the source of illumination gave the following results. In the presence of 15 cm. of oxygen, where the mol ratio of bromine to neopentane was 1:44, the reaction was complete in 6 hours; under the same conditions, save that the mol ratio was 1:2, no reaction occurred within two months.

^cTemperatures were 80° except where indicated.

^dQuantities expressed in mols per mol of bromine used. These experiments were performed at 50°. A blank run using carbon tetrachloride in place of neopentane gave no evidence of reaction.

in the dark. Oxygen alone has no effect in the light. At 80°, however, the reaction is slowly accelerated by increasing the con-

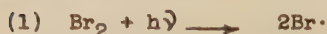
centration of oxygen in the light. There is no reaction when the oxygen is absent, whereas the reaction goes to completion when oxygen is present. Since only small quantities of material were used, the products of each reaction could not be identified. Attempts to prepare larger amounts of material by using more concentrated solutions of bromine in neopentane (1:2 moles respectively) resulted in no reaction even under optimum conditions.

Reformatsky⁶ was unable to obtain bromotrimethylacetic acid by the action of bromine on trimethylacetic acid or its acid chloride in the presence of phosphorus; at higher temperatures, a mixture of brominated hydrocarbons was obtained. In accord with these observations, it was found that bromine does not react with trimethylacetic acid under optimum conditions for the bromination of neopentane. At a temperature of 150°, a slow reaction takes place in the dark. An experiment using bromine and trimethylacetic acid in the molar ratio of 1:2 gave the following products: (1) hydrogen bromide, (2) carbon dioxide, (3) a mixture of brominated hydrocarbons, (4) nine per cent of a material identified as trimethylacetoxymethyltrimethylacetic acid, $(\text{CH}_3)_3\text{C}\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{C}(\text{CH}_3)_2\cdot\text{COOH}$. No carbon monoxide was formed in the reaction.

The side chain bromination of t-butyl benzene has not hitherto been reported. At 80° in the presence of oxygen and under illumination (the optimum conditions for the bromination of neopentane), only the nuclear brominated product was formed.

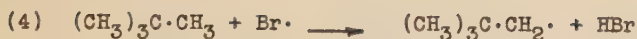
DISCUSSION

It is evident from the experiments just described that pure neopentane and bromine react slowly even under optimum conditions. The fact that the extremely slow reaction is accelerated by illumination and by oxygen or peroxides indicates a chain mechanism which may involve the following steps:



} Chain
initiating
reactions

⁶Reformatsky, Ber., 23, 1594 (1890).



The heat of reaction depends upon the position of the hydrogen atom replaced:

Hydrogen Atom	Heat of Replacement at 355° Abs. ⁷
Tertiary	16.0 kcal
Secondary	13.6 kcal
Primary	10.5 kcal

The difference between the tertiary and primary is 5.5 kcal. of which 4.4 kcal is due to the difference between the heats of formation of tertiary and primary hydrogen-carbon-bonds; the difference between the secondary and primary is 3.1 kcal. of which 2.6 is due to the difference between the heats of formation of secondary and primary hydrogen-carbon-bonds. Assuming that the heat of reaction is given by the difference between the energy of the bonds formed and the energy of those broken, it may readily be calculated that reaction (5) is probably exothermic, whereas reaction (4) probably requires considerable activation energy.

The fact that, at room temperature, tertiary and secondary hydrogen atoms are readily replaced by bromine, whereas primary hydrogen atoms are resistant to bromination indicates that the differences in energy of activation of tertiary, secondary, and primary hydrogen-carbon-bonds may critically affect the rate of reaction (4). At room temperature, these differences in the activation energy may limit the length of the chain in the given set of reactions, thus increasing the effects of the competing atom removing mechanisms. This explanation is significant in view of the retardation of the reaction by high bromine concentrations, which is especially marked in the reaction with neopentane.

Consideration of a similar chain mechanism in the chlorination of aliphatic hydrocarbons shows that the reaction corresponding to (4) would be exothermic, regardless of the nature of the alkyl radical. The activation energy for the step

⁷Conn, Kistiakowsky, and Smith, *J. Am. Chem. Soc.*, **60**, 2770 (1938).



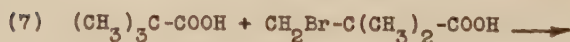
is probably so low that the strength of the hydrogen-carbon-bond should be unimportant, and such seems to be the fact. At higher temperatures the ratio of the amounts of chlorine substitution on primary, secondary, and tertiary carbon atoms closely approaches 1:1:1.⁸

In vapor phase bromination at high temperatures where bromine atoms may easily acquire the necessary activation energy, mixtures of normal and secondary brominated products are obtained.^{2b} In the present work an elevation in temperature was found necessary for the bromination of neopentane.

The ready bromination of toluene in the side chain, as contrasted to the exclusively nuclear bromination of t-butyl benzene, proves that in toluene the aliphatic hydrogen atoms are affected by the proximity of the phenyl group. A tentative explanation for this effect is that, since the benzyl radical formed in reaction (4) may be stabilized by resonance, less energy is required for the separation of an aliphatic hydrogen atom; hence the activation energy should be lower.

The bromination of acetic acid proceeds readily, whereas much difficulty is encountered in brominating trimethylacetic acid. Experiments conducted in this laboratory indicate that the bromination of propionic and n-butyric acid is photochemical and oxygen-catalyzed, whereas the bromination of acetic acid is little affected by light and oxygen. Obviously, the mechanism in the bromination of acetic acid is different from that in the bromination of other aliphatic acids.⁹

The formation of trimethylacetoxymethyltrimethylacetic acid at elevated temperatures (150°) suggests that this product is formed according to the reaction



⁸Haas, McBee, and Weber, *Ind. Eng. Chem.*, **28**, 333 (1936).

⁹Kharasch and Hobbs, Unpublished work.

EXPERIMENTAL PART

The neopentane used in this work was prepared by the method of Whitmore and Fleming.¹⁰ The final fractionation was kindly performed by the Universal Oil Products Company. A Raman spectrum examination made by Dr. Rosenbaum of this laboratory disclosed the presence of small amounts of unsaturated material. Further purification was effected by adding 1% of bromine to the neopentane in a bomb tube which was then sealed off in the presence of air. The tube was then placed about one centimeter from a mercury arc which warmed its contents to approximately 80°. Additions of 1% of bromine were continued until the color disappeared very slowly and uniformly. The product was then allowed to distill through wash towers filled respectively with concentrated sulfuric acid and 50% potassium hydroxide. It was finally passed through a tube containing calcium chloride. Fractionation gave two portions boiling between 9.4-9.5°; they had identical physical properties: n_D^{20} , 1.3515, melting point, -15.9°.

Tert-butyl benzene was obtained from Dr. H. C. Brown.¹¹ It was distilled prior to use. n_D^{20} , 1.4925; boiling point 166.5-166.8° at 730 mm.

Trimethylacetic acid was prepared according to Sandborn and Bousquet.¹² It was distilled prior to use. Boiling point 66-68° at 10 mm.; melting point 34.5-35.0°.

The bromine used was of purified analytical grade.¹³

The apparatus used was similar to that previously employed for the bromination of cyclopropane.¹³ However, instead of weighing the bromine sample, 0.064 ± 0.001 gram of bromine was delivered from a gas measuring bulb maintained at 25°. The neopentane was distilled into a small tank which was attached to the vacuum line by a brass to glass ground joint. For each experiment, the gas was collected in a small tube calibrated at 0° to deliver 1.227 grams of neopentane. The resulting mol fraction of bromine in

¹⁰ Whitmore and Fleming, J. Am. Chem. Soc., **55**, 3803 (1933).

¹¹ Kharasch and Brown, ibid., **61**, 2146 (1939).

¹² Organic Synthesis, Collective Vol. I, p. 512.

¹³ Kharasch, Fineman, and Mayo, J. Am. Chem. Soc., **61**, 2139 (1939).

neopentane was 0.0223.

For the dark reaction, the tubes were placed in pipes and kept in a thermostat at the proper temperature, whereas, for the light reaction, the liquid phase was exposed to a 500-watt incandescent lamp at a distance of ten centimeters. The extent of reaction was determined within an accuracy of 5% by comparison with color standards. Trimethylacetic acid (0.0196 moles) or t-butylbenzene (0.0172 moles) were added to the bomb tubes before they were sealed to the line. Where large concentrations of bromine were used, the bromine was measured directly into the reaction tube.

Trimethylacetoxymethylacetic acid.--A mixture consisting of 26 grams of trimethylacetic acid and 20 grams of bromine was heated to 150° in a bomb tube in the dark. When the bromine color disappeared, the tube was cooled in liquid nitrogen and then opened. Hydrogen bromide and carbon dioxide were allowed to boil off, and the residue was made alkaline with aqueous alkali. The water insoluble material was removed with ether. The aqueous portion was then acidified and extracted with ether. The ethereal extract was dried over calcium chloride and distilled. After removal of the ether and unreacted trimethylacetic acid, two grams of material boiling at 180-5° at 25 mm. was collected; this substance crystallized on standing. When recrystallized from ligroin, it formed long needles which showed parallel extinction and melted at 73.5°.

	Calculated for $C_{10}H_{18}O_4$	Found
% C	59.4	58.7
% H	9.0	9.2
Neutral equivalent	202	202.5
Saponification equivalent	202	196

Hydrolysis of the material and micro distillation gave one fraction which was identified as trimethylacetic acid. It melted at 34° and did not lower the melting point of a known sample of trimethylacetic acid. The other fraction was hydroxytrimethylacetic acid. It crystallized in needles from ether-ligroin mixture and melted at 123-4° (reported 125°). Its neutral equivalent was 120 (calculated 118). Its acetyl derivative melted at 55° (reported 56°). The reaction product is therefore trimethylacetoxymethylacetic acid in 9% yield.

SUMMARY

1. Bromine does not react with neopentane at 80° .
2. Oxygen has no effect on the reaction of bromine with neopentane at room temperature. At 80° it causes a slow reaction.
3. Organic peroxides have an effect on the bromination similar to that of oxygen, but begin to show this effect at 50° .
4. Tert-butylbenzene when treated with bromine shows only nuclear bromination.
5. A temperature of 150° is necessary for the reaction of bromine and trimethylacetic acid. The only products containing bromine are brominated hydrocarbons.

